



An efficient Cu-K-La/ γ -Al₂O₃ catalyst for catalytic oxidation of hydrogen chloride to chlorine

Kanka Feng^a, Chenwei Li^a, Yanglong Guo^{a,*}, Wangcheng Zhan^a, Binqun Ma^b, Binwu Chen^b, Maoquan Yuan^b, Guanzhong Lu^{a,*}

^a Key Laboratory for Advanced Materials, Research Institute of Industrial Catalysis, East China University of Science and Technology, Shanghai 200237, PR China

^b Shanghai Chlor-Alkali Chemical Co., Ltd., Shanghai 200241, PR China

ARTICLE INFO

Article history:

Received 10 June 2014

Received in revised form

22 September 2014

Accepted 24 September 2014

Available online 2 October 2014

Keywords:

Catalytic oxidation

Hydrogen chloride

Chlorine

Copper-based catalyst.

ABSTRACT

An efficient Cu-K-La/ γ -Al₂O₃ catalyst, prepared by the incipient wetness impregnation method, was developed for the catalytic oxidation of HCl to chlorine, in which effects of catalyst composition, calcination temperature, reaction temperature and GHSV of the feed gas and the catalyst stability were investigated. Cu-K-La/ γ -Al₂O₃ catalyst shows good catalytic performance and stability with the conversion of HCl of about 78% for reaction for over 9600 h under the reaction conditions of 30 g catalyst, 0.1 MPa, 340 °C, GHSV of 450 L/(kgcat h), HCl/O₂ = 2:1. Thermogravimetry results indicate that the synergistic promoters of KCl and LaCl₃ can significantly reduce the reaction temperature for oxidation of CuCl₂ to produce chlorine, which is a key step in the catalytic oxidation of HCl. XRD results show that there were only broad characteristic diffraction peaks of γ -Al₂O₃ support and copper species, potassium species and lanthanum species were highly dispersed on the surface of γ -Al₂O₃ support over Cu-K-La/ γ -Al₂O₃ catalyst.

© 2014 Elsevier B.V. All rights reserved.

1. Introduction

Toluene diisocyanate (TDI) and methylene diphenyl diisocyanate (MDI), key raw materials for manufacture of polyurethanes, are usually produced by phosgenation of the corresponding diamine precursors, in which chlorine reacts with carbon monoxide to produce phosgene. In manufacture of TDI or MDI, the byproduct of HCl is produced four times the molar amount of TDI or MDI. The demands for TDI and MDI are increasing sharply, which results in the inevitable production of much excessive HCl more than its market demand, serious disposal problem of toxic waste and thus cannot meet the increasingly stringent environmental regulations. Therefore, more strategies have been pursued to develop an efficient method for recycling chlorine from HCl to design a closed recycle process in the chlorine-related industries [1–4].

The processes recycling chlorine from HCl include three processes as follows [5,6]: (1) Electrolysis of HCl to produce Cl₂ and H₂ with the disadvantage of the electrodes generating great amounts of CO₂ equivalent due to their large electricity consumption. (2)

Cyclic oxidation of HCl by sulfuric acid as a circulating cyclic medium under a nitrogen oxide catalyst with very high capital cost due to the complexity of the process. (3) Catalytic oxidation of HCl to chlorine by air or O₂ (so-called Deacon process) over Cu-Dy-K/SiO₂ catalyst (Shell-Chlor process) [7], Cr₂O₃/SiO₂ (MT-Chlor process) [8], RuO₂/rutile-TiO₂ catalyst (Sumitomo process) [5] and RuO₂/SnO₂-Al₂O₃ catalyst (Bayer process) [9,10]. Deacon process has attracted increasing attention because of its relative ease of application, lower energy consumption and thermal requirements. Moreover, the catalytic oxidation of HCl is mildly exothermic reaction and thus lower reaction temperature is favorable for increasing the equilibrium conversion. Many efforts have been made for developing more efficient catalysts for the catalytic oxidation of HCl. Supported CeO₂ catalyst showed the conversion of HCl of 70–75% for over 700 h under the reaction conditions of the molar ratio of O₂ to HCl of 4.15, T_{inlet} = 633 K and P = 1 bar [11,12]. CuAlO₂ catalyst showed the conversion of HCl of about 25% for over 1200 h under the reaction conditions of the molar ratio of O₂ to HCl of 4, $W/F_{0(HCl)}$ = 8.96 g h mol^{−1}, T = 653 K and P = 1 bar [13,14]. RuO₂/SnO₂-Al₂O₃ catalyst showed the conversion of HCl of about 40% for 7000 h under the reaction conditions of the molar ratio of O₂ to HCl of 0.5, $W/F_{0(HCl)}$ = 36.4 g h mol^{−1}, T = 553–653 K and P = 0.1 MPa [9,10]. RuO₂/rutile-TiO₂ catalyst showed the conversion of HCl of 85–90% for 15,000 h [5].

* Corresponding authors. Tel./fax: +86 21 64252923.

E-mail addresses: yguo@ecust.edu.cn (Y. Guo), gzhlu@ecust.edu.cn (G. Lu).

Ruthenium-based catalysts are efficient commercialized catalysts for Deacon process; however, the high and dramatically fluctuating market price of ruthenium will limit the large-scale industrialization in the future, so it is necessary to develop other non-noble metal catalysts with low cost to replace the ruthenium-based catalysts [2,15,16]. The copper-based catalyst, invented for the first time by Deacon [17], was used for the catalytic oxidation of HCl to chlorine with the reaction temperature range of 430–475 °C. Nevertheless, copper chloride starts to evaporate at an appreciable rate above 400 °C, which results in the rapid deactivation of the copper-based catalyst. Lanthanum is often used to modify Cu/Al₂O₃ catalysts [18–20], in which La has particular functions in minimizing the formation of copper-aluminate and improving the thermal stability of alumina support, increasing the dispersion degree of Cu species and inhibiting the sintering of Cu species. In this work, Cu-K-La/γ-Al₂O₃ catalyst was developed for the catalytic oxidation of hydrogen chloride to chlorine, in which effects of catalyst composition, calcination temperature, reaction temperature and GHSV of the feed gas, and the catalyst stability for over 9600 h were investigated.

2. Experimental

2.1. Preparation of Cu-K-La/γ-Al₂O₃ catalyst

Cu-K-La/γ-Al₂O₃ catalyst was prepared by the incipient wetness impregnation method in our previous work [21], in which the weight ratio of CuCl₂, KCl and LaCl₃ was 3:1:2, and the total loading amount of the chloride precursors were 15, 20, 25, 30 and 35 wt%, respectively. The aqueous solution containing the above chloride precursors was added dropwise into γ-Al₂O₃ spherical support with 2.0 mm diameter, and then the sample was dried at 120 °C for 12 h and calcined at 400 °C in air for 4 h.

2.2. Characterization of Cu-K-La/γ-Al₂O₃ catalyst

Thermogravimetry (TG) was carried out on a Perkin Elmer Pyris Diamond TG-DTA analyzers, in which the sample was heated from 40 to 800 °C at the rate of 10 °C min⁻¹ in the atmosphere of air of 100 mL min⁻¹.

TGA-MS profiles of the as-prepared and non-calcined CuCl₂-KCl-LaCl₃/γ-Al₂O₃ sample were carried out on a Perkin Elmer Pyris 1 thermogravimetric analyzer and Hiden HPR 20 mass spectrometer, in which the sample was heated from 40 to 850 °C at the rate of 10 °C min⁻¹ in the atmosphere of air of 30 mL min⁻¹.

The powder XRD patterns were recorded on a Bruker AXS D8 Focus diffractometer operated at 40 kV, 40 mA (Cu Kα radiation, λ = 0.15406 nm), and the diffraction patterns were taken in the range of 10° < 2θ < 80° at the scanning rate of 6° min⁻¹.

2.3. Catalytic oxidation of HCl

The catalytic oxidation of HCl over Cu-K-La/γ-Al₂O₃ catalyst was investigated in the quartz fixed-bed reactor under the reaction conditions of 30 g catalyst, 0.1 MPa, GHSV of 450 L/(kgcat h), HCl/O₂ = 2:1 (molar ratio). The flow rate of HCl and O₂ was 150 and 75 mL min⁻¹, respectively, which were introduced into the reactor by the mass flow controllers. The product of chlorine was analyzed by iodometry method and the excess hydrogen chloride was quantified by the standard sodium hydroxide solution. There was no byproduct in the catalytic oxidation of HCl, therefore the selectivity of chlorine was 100%, and the value of the conversion of HCl was equal to that of the yield of chlorine.

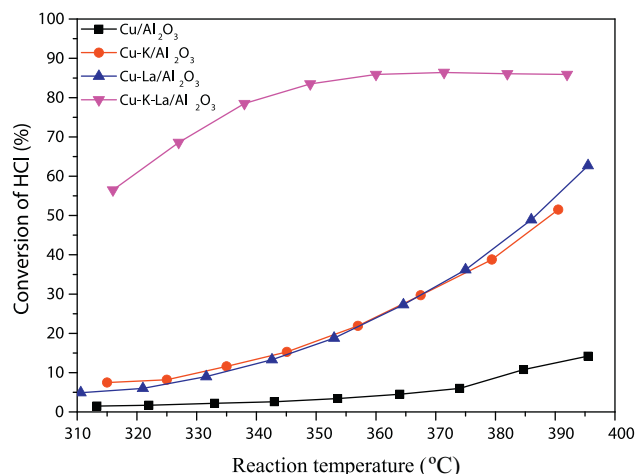


Fig. 1. Catalytic performance of the copper-based catalysts with different catalyst compositions for HCl oxidation.

3. Results and discussion

3.1. Catalytic oxidation of HCl

3.1.1. Effect of catalyst composition

Fig. 1 shows the catalytic performance of the copper-based catalysts with different catalyst compositions for HCl oxidation. As shown in Fig. 1, Cu/γ-Al₂O₃ catalyst had the worst catalytic activity with the maximum conversion of HCl of 14.2% at 396 °C. Both Cu-K/γ-Al₂O₃ and Cu-La/γ-Al₂O₃ catalysts had better catalytic activities than Cu/γ-Al₂O₃ catalyst, which increased greatly with an increase in the reaction temperature. Cu-K-La/γ-Al₂O₃ catalyst had the best catalytic activity among the above-mentioned copper-based catalysts, in which when the reaction temperature was higher than 360 °C, the conversion of HCl reached the similar value of about 86% due to the thermodynamic-controlled Deacon reaction at higher reaction temperatures. These results indicate that the significant increase in the catalytic activity of Cu-K-La/γ-Al₂O₃ catalyst is due to the synergistic promotion effect of KCl and LaCl₃.

Fig. 2 shows the effect of the total loading amount of the chloride precursors (CuCl₂, KCl and LaCl₃) on the conversion of HCl over Cu-K-La/γ-Al₂O₃ catalyst for HCl oxidation. As shown in Fig. 2, with an increase in the total loading amount of the chloride precursors,

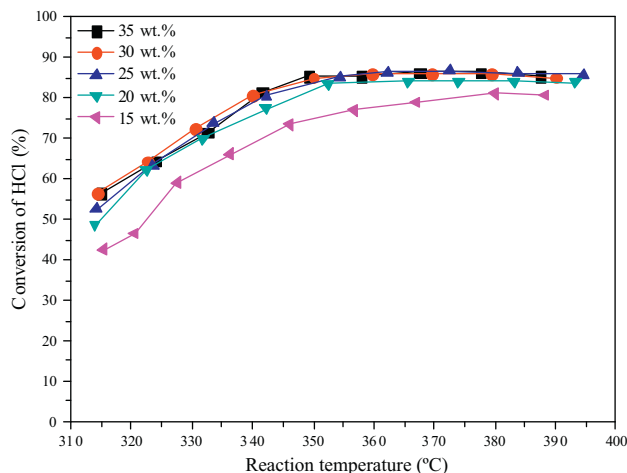


Fig. 2. Effect of the total loading amount of the chloride precursors on the conversion of HCl over Cu-K-La/γ-Al₂O₃ catalyst for HCl oxidation.

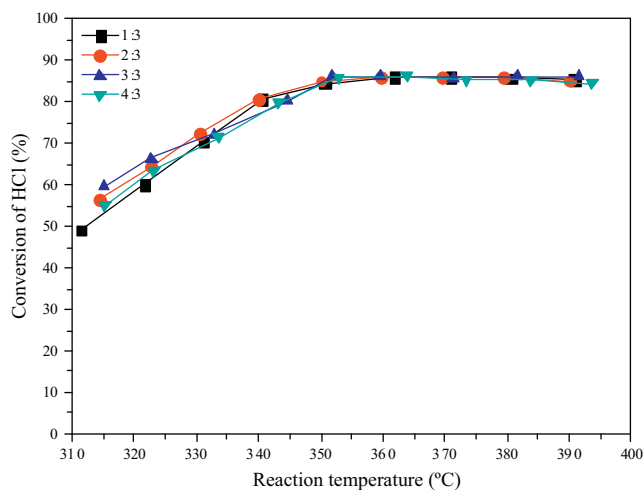


Fig. 3. Effect of the mass ratio of LaCl_3 to CuCl_2 on the conversion of HCl over Cu-K-La/ $\gamma\text{-Al}_2\text{O}_3$ catalyst for HCl oxidation.

the conversion of HCl over Cu-K-La/ $\gamma\text{-Al}_2\text{O}_3$ catalyst increased till the total loading amount reached 30 wt% and then kept constant. With increasing the reaction temperature, the conversion of HCl over all Cu-K-La/ $\gamma\text{-Al}_2\text{O}_3$ catalysts increased and then remained constant. When the reaction temperature was higher than 350 °C and the total loading amount was more than 25 wt%, the conversion of HCl over Cu-K-La/ $\gamma\text{-Al}_2\text{O}_3$ catalysts reached the similar values. Deacon process is exothermic reaction, and lower reaction temperature is favorable for increasing the equilibrium conversion, but this Deacon reaction is kinetics-controlled reaction at lower reaction temperatures and thermodynamic-controlled reaction at higher reaction temperatures [1]. Therefore, the optimum value of the total loading amount of the chloride precursors of Cu-K-La/ $\gamma\text{-Al}_2\text{O}_3$ catalyst was more than 25 wt%.

Fig. 3 shows the effect of the mass ratio of LaCl_3 to CuCl_2 on the conversion of HCl over Cu-K-La/ $\gamma\text{-Al}_2\text{O}_3$ catalyst with the total loading amount of the chloride precursors of 30 wt% for HCl oxidation. As shown in Fig. 3, when the mass ratio of LaCl_3 to CuCl_2 was 2:3, the conversion of HCl over Cu-K-La/ $\gamma\text{-Al}_2\text{O}_3$ catalyst was highest. With increasing reaction temperature, the differences in the conversion of HCl over all catalysts were diminished gradually and the conversion of HCl remained the same when the reaction temperature was higher than 350 °C. Therefore, the optimum value of the mass ratio of LaCl_3 to CuCl_2 of Cu-K-La/ $\gamma\text{-Al}_2\text{O}_3$ catalyst was 2:3.

3.1.2. Effect of calcination temperature

Fig. 4 shows the effect of the calcination temperature on the conversion of HCl over Cu-K-La/ $\gamma\text{-Al}_2\text{O}_3$ catalyst with the total loading amount of the chloride precursors of 30 wt% for HCl oxidation. As shown in Fig. 4, with an increase in the calcination temperature, the conversion of HCl over Cu-K-La/ $\gamma\text{-Al}_2\text{O}_3$ catalyst increased gradually and reached a maximum till the calcination temperature at 400 °C, then declined gently. Therefore, the optimum value of the calcination temperature for Cu-K-La/ $\gamma\text{-Al}_2\text{O}_3$ catalyst was 400 °C.

3.1.3. Effect of GHSV of the feed gas

Fig. 5 shows the effect of GHSV of the feed gas on the production rate of chlorine over Cu-K-La/ $\gamma\text{-Al}_2\text{O}_3$ catalyst for HCl oxidation. As shown in Fig. 5, the production rate of chlorine had good linear relationship with GHSV of the feed gas, that is, to say, with increasing GHSV of the feed gas from 150 to 1200 L/(kgcat h), the production rate of chlorine increased linearly from 2.1 to 14.3 mol_{Cl₂}/(kgcat h), which indicates that Cu-K-La/ $\gamma\text{-Al}_2\text{O}_3$ catalyst can provide enough

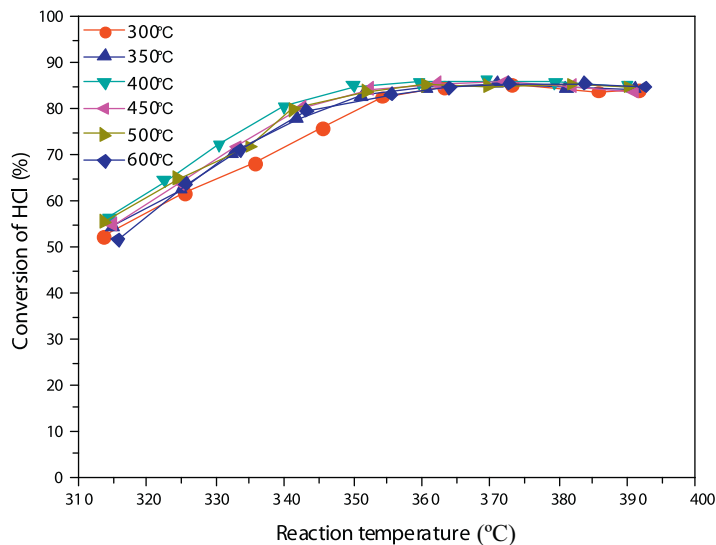


Fig. 4. Effect of the calcination temperature on the conversion of HCl over Cu-K-La/ $\gamma\text{-Al}_2\text{O}_3$ catalyst for HCl oxidation.

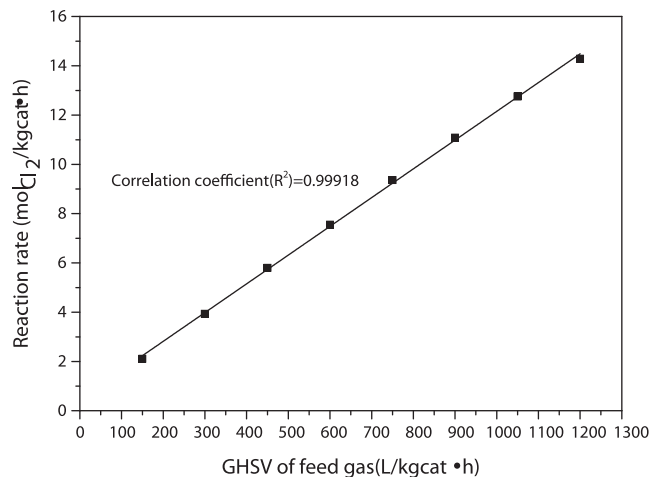


Fig. 5. Effect of GHSV of the feed gas on the production rate of chlorine over Cu-K-La/ $\gamma\text{-Al}_2\text{O}_3$ catalyst for HCl oxidation.

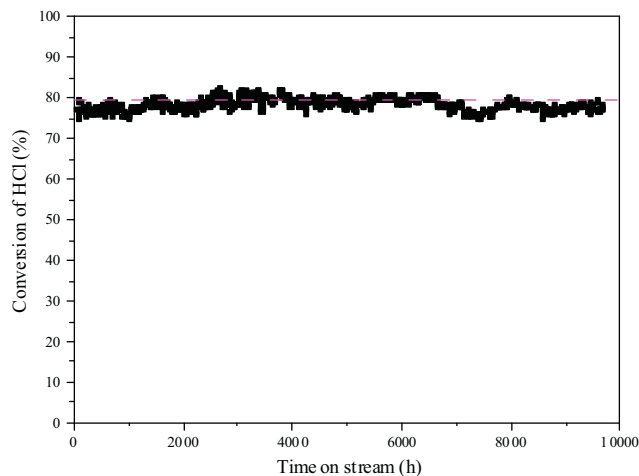


Fig. 6. The stability of Cu-K-La/ $\gamma\text{-Al}_2\text{O}_3$ catalyst for HCl oxidation.

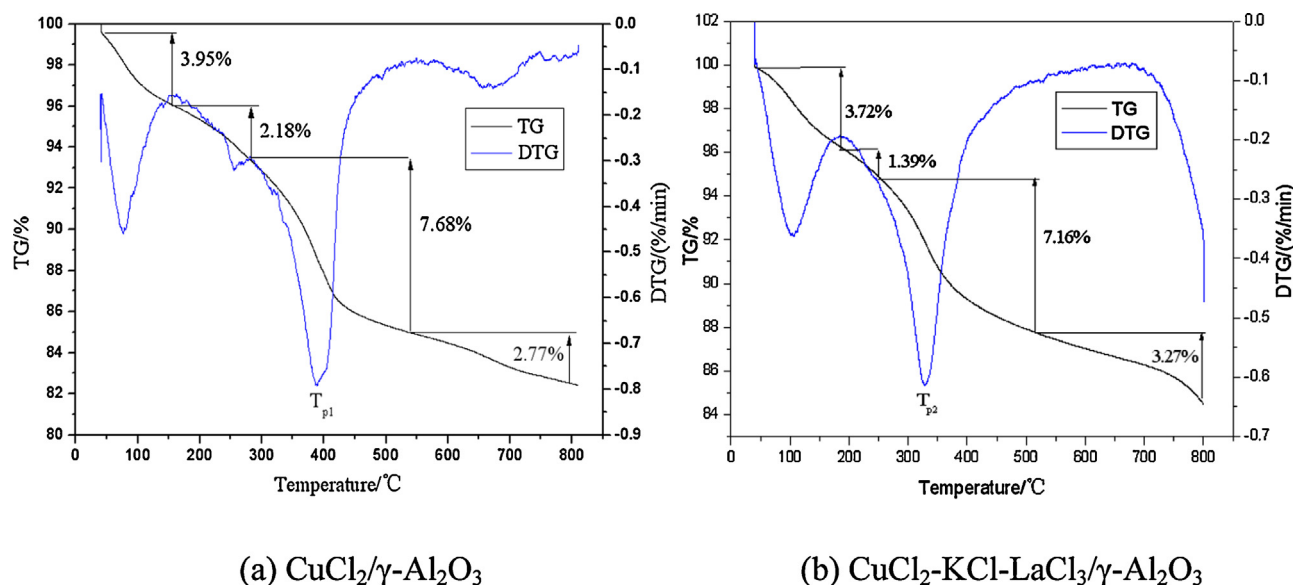


Fig. 7. TG profiles of as-prepared and non-calcined $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ and $\text{CuCl}_2\text{-KCl-LaCl}_3/\gamma\text{-Al}_2\text{O}_3$ samples.

active sites for HCl oxidation even under higher GHSV of the feed gas. Therefore, $\text{Cu-K-La}/\gamma\text{-Al}_2\text{O}_3$ catalyst shows good catalytic performance over wide range of GHSV of the feed gas.

3.1.4. The catalyst stability

Fig. 6 shows the stability of $\text{Cu-K-La}/\gamma\text{-Al}_2\text{O}_3$ catalyst with the total loading amount of the chloride precursors of 30 wt% for HCl oxidation for over 9600 h. As shown in Fig. 6, the conversion of HCl was 75–82% and the average conversion of HCl was about 78% for 9600 h, and there was little change in the conversion of HCl for reaction for over 9600 h. The test of this catalyst stability is still under operation and the demonstration plant of 1000 T/a of chlorine is under construction. Therefore, $\text{Cu-K-La}/\gamma\text{-Al}_2\text{O}_3$ catalyst shows excellent stability.

3.2. TG

Fig. 7 shows the TG profiles of as-prepared and non-calcined $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ and $\text{CuCl}_2\text{-KCl-LaCl}_3/\gamma\text{-Al}_2\text{O}_3$ samples. As shown in Fig. 7, there were four peaks of weight loss. The first peak of weight loss was attributed to desorption of the physically adsorbed water, the second peak was attributed to the desorption of the chemically adsorbed water and the fourth peak may be attributed to the dehydroxylation of $\gamma\text{-Al}_2\text{O}_3$ support. The third main peak of weight loss was attributed to the process in which copper chloride reacted with oxygen to become copper oxide and release chlorine. Over $\text{CuCl}_2\text{-KCl-LaCl}_3/\gamma\text{-Al}_2\text{O}_3$ sample, the peak temperature of the third peak of weight loss shifted to lower temperature at the difference of 62 °C, which indicated that the synergistic promoters of KCl and LaCl_3 could significantly reduce the reaction temperature for the oxidation reaction of CuCl_2 to produce chlorine, a key step in the catalytic oxidation of HCl. The catalytic oxidation of HCl is an exothermic reaction, and hence lower reaction temperature is favorable for increasing the equilibrium conversion. Over the $\text{CuCl}_2/\gamma\text{-Al}_2\text{O}_3$ sample, the peak temperature of the third peak of weight loss was 392 °C, and the reaction temperature for HCl oxidation was over 400 °C, which made copper chlorides easily volatile and thus decreased the catalyst stability. Over the $\text{CuCl}_2\text{-KCl-LaCl}_3/\gamma\text{-Al}_2\text{O}_3$ sample, the peak temperature of the third peak of weight loss was 330 °C, and the reaction temperature for HCl oxidation was above 340 °C, which increased the conversion of HCl and made the catalyst more stable.

4. Conclusions

$\text{Cu-K-La}/\gamma\text{-Al}_2\text{O}_3$ catalyst shows good catalytic performance over wide range of GHSV of the feed gas and excellent catalyst stability for over 9600 h for the catalytic oxidation of hydrogen chloride to chlorine. Under the reaction conditions of 0.1 MPa, 340 °C, GHSV of 450 L/(kgcat h) and $\text{HCl}/\text{O}_2 = 2:1$, the average conversion of HCl was about 78% for 9600 h, and there was little change in the conversion of HCl for reaction for over 9600 h over $\text{Cu-K-La}/\gamma\text{-Al}_2\text{O}_3$ catalyst, in which the total loading amount of the chloride precursors was 30 wt%, and the weight ratio of CuCl_2 , KCl and LaCl_3 was 3:1:2. The TG results indicate that the synergistic promoters of KCl and LaCl_3 can significantly reduce the reaction temperature for the oxidation reaction of CuCl_2 to produce chlorine, a key step in the catalytic oxidation of HCl to chlorine, which is favorable for increasing the equilibrium conversion and the catalyst stability due to the exothermic oxidation reaction of HCl to chlorine. The XRD results show that copper species, potassium species and lanthanum species were highly dispersed on the surface of $\gamma\text{-Al}_2\text{O}_3$ support over the $\text{Cu-K-La}/\gamma\text{-Al}_2\text{O}_3$ catalyst.

Acknowledgements

This project was supported by the National Basic Research Program of China (2010CB732300), Commission of Science and Technology of Shanghai Municipality (13521103402), Shu Guang Project of Shanghai Municipal Education Commission and Shanghai Education Development Foundation (10SG30).

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2014.09.063>.

References

- [1] M. Mortensen, R.G. Minet, T.T. Tsotsis, S.W. Benson, *Chem. Eng. Sci.* 54 (1999) 2131–2139.
- [2] J. Perez-Ramirez, C. Mondelli, T. Schmidt, O.F.K. Schlüter, A. Wolf, L. Mleczko, T. Dreier, *Energy Environ. Sci.* 4 (2011) 4786–4799.
- [3] D. Crihan, M. Knapp, S. Zweidinger, E. Lundgren, C.J. Weststrate, J.N. Andersen, A.P. Seitsonen, H. Over, *Angew. Chem. Int. Ed. Engl.* 47 (2008) 2131–2134.

- [4] N. Lopez, J. Gomez-Segura, R.P. Marin, J. Perez-Ramirez, *J. Catal.* 255 (2008) 29–39.
- [5] K. Seki, *Catal. Surv. Asia* 14 (2010) 168–175.
- [6] H.Y. Pan, R.G. Minet, S.W. Benson, T.T. Tsotsis, *Ind. Eng. Chem. Res.* 33 (1994) 2996–3003.
- [7] A.J. Johnson, A.J. Cherniavsky, US Patent 2,542,961 (1951).
- [8] T. Kiyoura, Y. Kogure, T. Nagayama, K. Kanaya, US Patent 4,822,589 (1989).
- [9] C. Mondelli, A.P. Amrute, F. Krumeich, T. Schmidt, J. PerezRamírez, *ChemCatChem* 3 (2011) 657–660.
- [10] A.P. Amrute, C. Mondelli, T. Schmidt, R. Hauert, J. PerezRamírez, *ChemCatChem* 5 (2013) 748–756.
- [11] A.P. Amrute, C. Mondelli, M. Moser, G. Novell-Leruth, N. Loípez, D. Rosenthal, R. Farra, M.E. Schuster, D. Teschner, T. Schmidt, J. Pérez-Ramírez, *J. Catal.* 286 (2012) 287–297.
- [12] M. Moser, C. Mondelli, T. Schmidt, F. Girgsdies, M.E. Schuster, F. Farra, L. Szentmiklósi, D. Teschner, J. Pérez-Ramírez, *Appl. Catal. B* 132–133 (2013) 123–131.
- [13] C. Mondelli, A.P. Amrute, T. Schmidt, J. Perez-Ramirez, *Chem. Commun.* 47 (2011) 7173–7175.
- [14] A.P. Amrute, G.O. Larrazabal, C. Mondelli, J. Perez-Ramirez, *Angew. Chem. Int. Ed. Engl.* 125 (2013) 1–5.
- [15] M. Hammes, M. Valtchev, M.B. Roth, K. Stöwe, W.F. Maier, *Appl. Catal. B* 132–133 (2013) 389–400.
- [16] H. Over, R. Schomäcker, *ACS Catal.* 3 (2013) 1034–1046.
- [17] H. Deacon, US Patent 85,370 (1868).
- [18] A.J. Rouco, *J. Catal.* 157 (1995) 380–387.
- [19] X.J. Lv, J. Liu, G.D. Zhou, K.J. Zhen, W.X. Li, T.X. Cheng, *Catal. Lett.* 100 (2005) 153–159.
- [20] N.B. Muddada, U. Olsbye, T. Fuglerud, S. Vidotto, A. Marsella, S. Bordiga, D. Gianolio, G. Leofanti, C. Lamberti, *J. Catal.* 284 (2011) 236–246.
- [21] K.K. Feng, C.W. Li, Y.L. Guo, W.C. Zhan, B.Q. Ma, B.W. Chen, M.Q. Yuan, G.Z. Lu, *Chin. J. Catal.* 35 (2014) 1359–1363.